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Dedicated to Professor Valer Farcasan
on the occasion of his 95th anniversary

EPINEPHRINE DETECTION AT Pt-NANOPARTICLES MODIFIED GRAPHITE ELECTRODE BY SQUARE-WAVE VOLTAMMETRY

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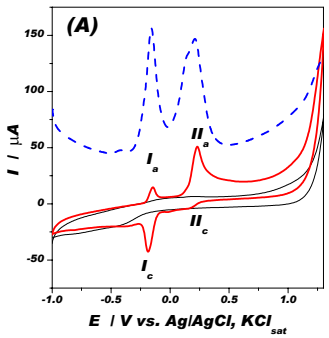
A G/PtNP-Chi modified electrode was prepared by immobilizing Pt-nanoparticles in a chitosan film. The investigation of the influence of the experimental conditions (scan rate, frequency, pH) on the electrochemical behaviour of epinephrine (EP) was realized by both cyclic and square-wave voltammetry. The electrochemical parameters and analytical parameters like high sensitivity and low detection limit of the G/PtNP-Chi modified electrode make it very suitable for accurate determinations in real samples of pharmaceutical formulation.



INTRODUCTION

According to their polyphenolic nature, catecholamines are a group of compounds exhibiting good natural antioxidants properties, by reacting rapidly with reactive oxygen species (ROS), and thus performing the decrease of ROS toxic action and preventing the radical chain process in organism. Their antioxidant effect can be due to both (i) the radical scavenging activity and (ii) to the metal-chelating properties.[1] The presence of conjugate benzene rings and hydroxyl groups can give rise to antioxidant function of the compounds having applications for *in vitro* studies or as elements of free systems during scavenging peroxide anions, oxygen singlets, peroxide radicals of lipids and free radical stabilisation in oxidation processes through hydrogenation.[2]

Epinephrine (EP) or adrenaline, a hormone belonging to catecholamine group, is an important neurotransmitter in the mammalian central nervous system and plays a very important role in the function of central nervous, renal, hormonal, and cardiovascular systems. Commonly, EP is used as a vasoconstrictor, cardiac stimulator and bronchodilator drug to treat anaphylactic shock,

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bronchial asthma and organic heart disease.[3] It exits in the nervous tissue and body fluid in the form of large organic cations, which subsists in protonated form at physiological pH.[4,5] Because the change of catecholamine concentration is a subject of great significance in neurophysiology (neurological disorders such as Parkinson's), clinical diagnosis and quality control in drugs, the development of quantitative methods for their detection, is necessary in view to study their physiological function (canvassing of neuro-transmission) and to diagnose and cure diseases in clinical medicine field.[6]

Usually, the analysis of EP is carried out by methods like: chromatography,[7-10] capillary electro-phoresis,[11-13] fluorescence,[9,14] electro/chemilumines-cence,[15,16] flow injection analysis,[17-19] spectro-photometry,[20,21] and electrochemical detection.[22] All these methods require expensive instruments, well-controlled experimental conditions and long-time sample-preparation.

Consequently, electroanalytical methods have gained wide popularity in recent years in comparison with the sophisticated methods named above, because of their simplicity, speed and sensitivity, low cost and a small number of required samples. The major drawback to detect EP by using electrochemical methods was encountered when metallic electrodes were used because of: (i) interference from ascorbic acids (AA) and uric acids (UA), both of which largely coexist with neurotransmitters in body fluids and having a nearly identical oxidation potential range on the plain electrodes;[3] (ii) electron transfer rate of oxidation process of EP to quinone is so slow that it is often adsorbed on the surface of electrode, resulting in its passivation.[23]

Therefore, in view to obtain the selective detection of EP, it were developed new materials as modified electrode using: nanoparticles,[3,24] carbon nanotubes,[3,4,25-28] polymers,[25;29-35] graphene/ gold nanocomposites,[36] dye doped sol–gel,[37] conduc-tive diamond electrodes,[38] organic modifier,[39,40] and inorganic modifier.[4,27,41-43]

The aim of this work was the study of the influence of the experimental conditions (scan rate, frequency, pH) on the electrochemical behaviour of epinephrine at bare and Pt-nanoparticles (PtNP) modified graphite electrode, by both cyclic and square-wave voltammetry, in view to estimate the characteristic electrochemical parameters for explain the mechanism of the redox process. The PtNP modified electrode was used in the detection of epinephrine in real sample (epinephrine ampoules).

EXPERIMENTAL

Reagents

The (*R)*-4-(1-hidroxi-2-(metilamino)etil)benzen-1,2-diol (epinephrine, EP) of p.a. quality was supplied by Sigma-Aldrich GmbH and the corresponding 10^{-3} M solution was prepared in 0.1 M phosphate buffer solution (pH 7). Also, 2-amino-2-deoxy-(1→4)-β-D-glucopyranan (chitosan, Chi) and acetic acid (99.7%) were purchased from Sigma-Aldrich GmbH and Reactivul Bucuresti, respectively. Nanoparticles of Pt stabilised on graphite powder (PtNP) were a kindly gift from dr. Dan Goia (Clarkson University, Potsdam, USA) and is greatly acknowledged here. The appropriate amounts of Na_2HPO_4, NaH_2PO_4, supplied also by Sigma-Aldrich GmbH, were used for preparing the 0.1 M phosphate buffer solution. Phosphoric acid and NaOH solutions from Merck were used for adjusting the pH of electrolyte. Commercial epinephrine ampoules (1 mg/ml) were purchase from pharmacy.

Equipments

In order to assess the electrochemical behaviour of the investigated compounds cyclic voltammetry (CV) and square-wave voltammetry (SWV) methods were used, employing a computer controlled - Autolab analytical unit (PGStat10, EcoChemie, Holland). For measurements was used an undivided cell equipped with following three-electrodes: a graphite working electrode (Ringsdorff, Germany) (diameter 0.3 cm), an Ag/AgCl, KCl_{sat} reference electrode (Radiometer, France) and a Pt wire counter electrode. The working bare graphite electrode was mirror-polished with graded alumina powder (1 μm and 0.1 μm, Stuers, Copenhagen, Denmark) prior to each experiment.

Preparation of the G/PtNP-Chi electrode

The surface of the graphite electrode (G) was thoroughly polished on alumina slurry then rinsed with bidistilled water. The electrodes were sonicated for 5 minutes in acetone, in order to remove alumina particles and other possible contaminants. The PtNP were immobilized onto clean G electrode surface using a biodegradable polyelectrolyte matrix of chitosan (Chi). A chitosan solution was obtained by mixing 10 mg chitosan to 10 ml of 0.1 M acetic acid, followed by 30 min of sonication. A suspension of 1 mg of PtNP in 500 μl chitosan solution was strongly mixed by sonication, for 2 h. A volume of 5 μl of suspension was placed on the G surface, and was dried for 2 h, at room temperature, covered by a beaker in view to achieve a uniform PtNP-chitosan composite film on the electrode surface (G/PtNP-Chi).

RESULTS AND DISCUSSION

Electrochemical behaviour of epinephrine at G/PtNP-Chi modified electrode

The electrochemical redox reactions of 10^{-3} M epinephrine at the G and G/PtNP-Chi modified graphite electrode were studied by both cyclic voltammetry (CV) and square-wave voltammetry (SWV), as seen in Fig. 1 A, B.

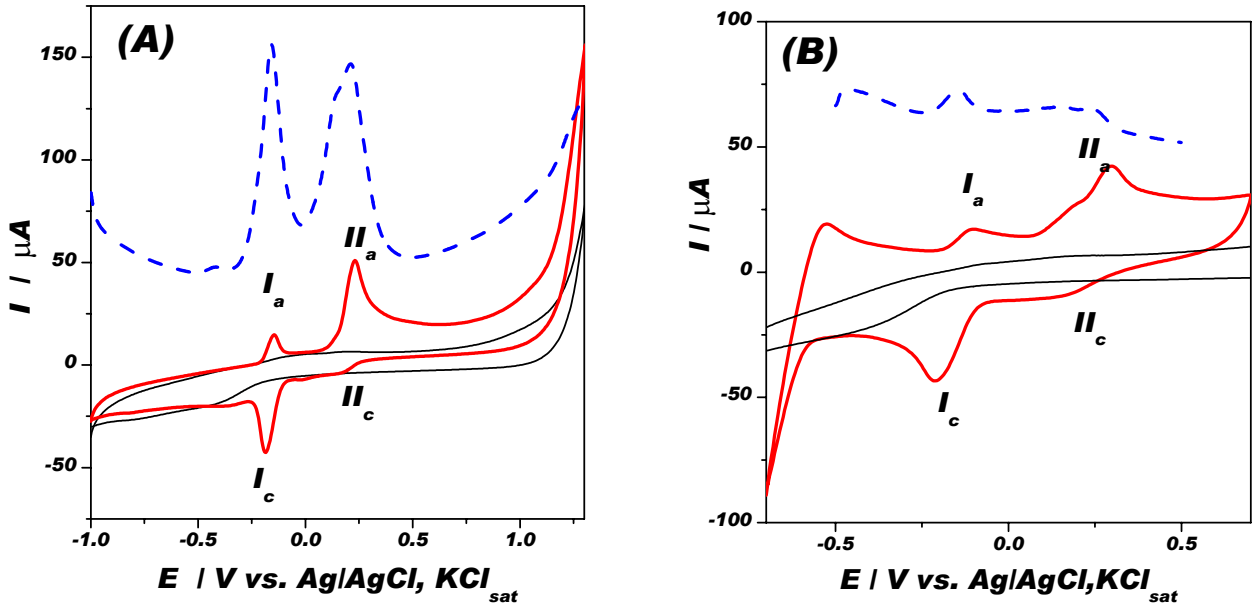
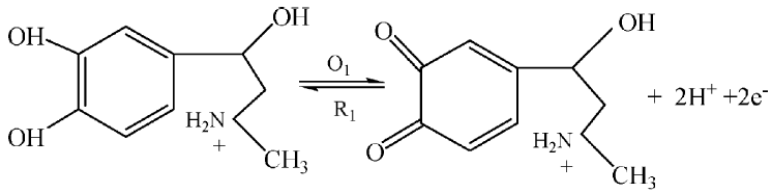


Fig. 1 – Cyclic (solid thick line) and square-wave (dash thick line) voltammograms of 10^{-3} M epinephrine at G (A) and G/PtNP-Chi (B) electrodes. Experimental conditions: electrolyte, 0.1 M phosphate buffer solution (pH 7) (solid thin line); starting potential, -1 V *vs.* Ag/AgCl,KCl_{sat}; scan rate, 50 mV/s (CV); step potential, 0.00195 V (SWV); amplitude, 0.050 V (SWV); frequency, 10 s^{-1} (SWV).

In the studied potential scan range, epinephrine exhibits two pairs of peaks (abbreviated I, II) on both G and G/PtNP-Chi investigated electrodes, while the electrolyte, as expected shows no peaks, except the charging of the electrical double layer (thin lines in Fig. 1 A, B).

At pH 7, regardless the type of used working electrode, the total redox process consists in the oxidation (two protons, two-electron) of epinephrine to its corresponding open chain quinone, following the reaction:[42]



epinephrine epinephrinequinone

Regardless of the type of electrode (*i.e.*, glassy carbon,[35] Al-incorporated mesoporous SiO_2,[42] platinum,[44] carbon nanotubes modified edge plane pyrolytic graphite electrode,[28] gold and modified Au electrode[6,40]) the mechanism of the oxidation reaction consists in the succession of chemical (C) and electrochemical (E) steps, namely a succession of ECCCEE steps, where the first E is assigned to IIa peak, followed by deprotonation (first C), cyclization (second C), and disproportionation (third C), and then again E (for Ic peak), and the final E (for Ia peak) as described in literature.[44]

The electrochemical parameters of the redox behaviour of the epinephrine at G and G/PtNP-Chi electrodes are summarized in Table 1. The analyze of the obtained date lead to conclude that for anodic peaks Ia/Ic or IIa/IIc obtained at G/PtNP-Chi electrode, the negative/positive values of potentials are shifted to more positive values than those obtained at G electrode for both CV or SWV investigations. Also, by CV at G/PtNP-Chi electrode, only the cathodic peak potential Ic is shifted to more negative values. The values of $E^{0'}$ for the two peaks of epinephrine at G and G/PtNP-Chi electrodes, respectively are quasi similarly, but the increase of the ΔE_p values for both peaks at G/PtNP-Chi electrode prove a best peak separation at this electrode, confirming a quasi-reversible redox electrode process. The I_{pa}/I_{pc} ratio at both electrode and peaks, respectively are either

smallest or greater than the theoretical value 1 for a diffusion controlled process, and as expected smallest in the case of G/PtNP-Chi electrode. Regardless the investigated electrode, because of the very small values of the current intensity of peak IIc, it can be considered that the process II corresponds to an irreversible oxidation step of epinephrine, at pH 7.

Influence of the scan rate and frequency

The influence of the experimental conditions (*i.e.*, scan rate for cyclic voltammetry and frequency for square wave voltammetry) are presented in Fig. 2A-B.

Regardless the studied electrode, with increasing of the scan rate, the peak current intensity is increasing and the corresponding Ia/Ic and IIa/IIc peak potentials are shifted towards positive and negative values, respectively (results not shown). At G and G/PtNP-Chi electrodes, the $\log(I_p/\mu A)$ - $\log(v/(V*s^{-1}))$ dependencies for each peak pairs (Ia/Ic and IIa/IIc) are linear with a slope close to 0.5 (see Table 2), proving that the redox behavior of the epinephrine occurs under diffusion control at pH 7, as described by the Randles-Sevcik equation.[45]

It is worth to mention that as expected, a decrease of the current intensities of peak pairs Ia/Ic and IIa/IIc at G/PtNP-Chi electrodes is obtained comparing with the bare G electrode, confirming that the PtNP-Chi matrix acts as a diffusion barrier for epinephrine towards electrode interface. The polymeric matrix of chitosan is sufficiently porous to ensure the diffusion of epinephrine to graphite surface (Fig. 2A).

Table 1

Electrochemical parameters for the redox behaviour of 10^{-3} M epinephrine. Experimental conditions: see Figure 1

Parameters	G electrode				G/PtNP-Chi electrode			
	CV, v = 50 mV/s		SWV, f = 10 s^{-1}		CV, v = 50 mV/s		SWV, f = 10 s^{-1}	
	Peak I	Peak II	Peak Ia	Peak IIa	Peak I	Peak II	Peak Ia	Peak IIa
E_{pa} / V *vs.* ER	-0.146	0.230	-0.160	0.210	-0.104	0.296	-0.147	0.226
E_{pc} /V *vs.* ER	-0.185	0.162	-	-	-0.212	0.164	-	-
$E^{0'}$ / V *vs.* ER*	-0.166	0.196	-	-	-0.158	0.230	-	-
ΔE_p / V *vs.* ER**	0.039	0.068	-	-	0.108	0.132		
I_{pa}/I_{pc}	0.41	15.4	-	-	0.23	4.84	-	-

where: $E^{0'} = (E_{pa} + E_{pc})/2$; $\Delta E_p = E_{pa} - E_{pc}$; where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential.

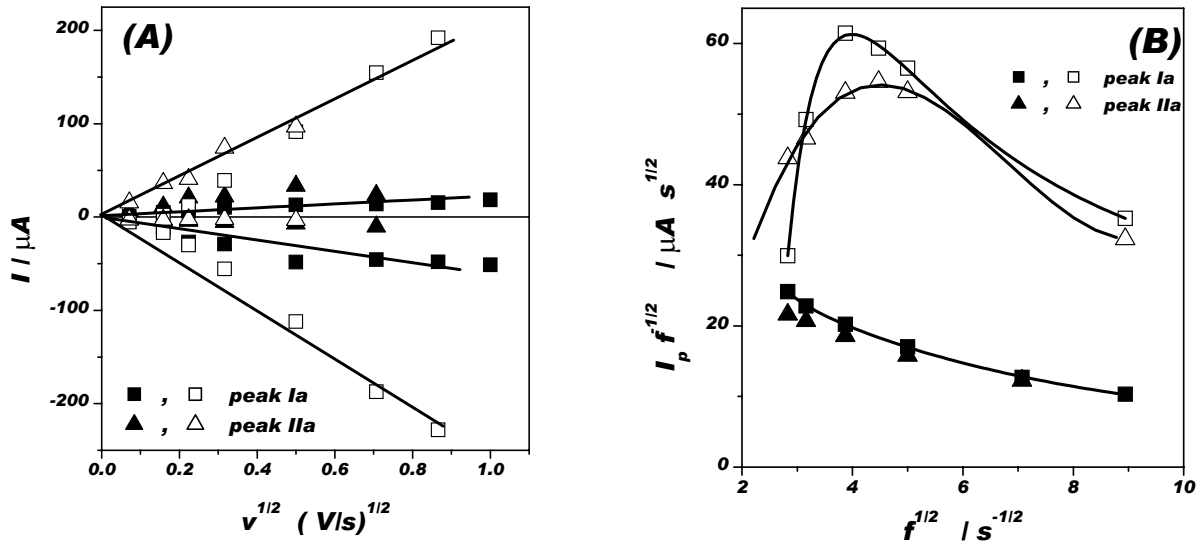


Fig. 2 – Influence of CV scan rate on the current intensity (A) and influence of SW frequency on the ratio of the SW peak current and the square root of the frequency (B) for the oxidation of 10^{-3} M epinephrine at G (□, Δ) and G/PtNP-chitosan (■, ▲) modified electrode. Experimental conditions: electrolyte, 0.1 M phosphate buffer (pH 7), starting potential, -1 V *vs.* Ag/AgCl,KCl_{sat}; step potential, 0.002 V (SWV); amplitude, 0.050 V (SWV).

Table 2

Slope of $\log(I_p/\mu A)$ - $\log(v/(V*s^{-1}))$ dependencies for the redox behaviour of 10^{-3} M epinephrine. Experimental conditions: see Figure 1

Process	G electrode		G/PtNP-Chi electrode	
	Peak I	Peak II	Peak Ia	Peak IIa
Anodic R/n	-	0.476 ± 0.040 0.9892/5	0.473 ± 0.059 0.9551/8	0.342 ± 0.076 0.9142/6
Cathodic R/n	0.760 ± 0.015 0.9989/7	-	0.434 ± 0.058 0.9497/8	0.291 ± 0.025 0.9852/6

For studying the influence of the frequency in SWV, Mirceski and co-workers proposed a model consisting in the dependence of $I_p f^{-1/2}$ *vs.* $f^{1/2}$, which either show a well-defined maximum corresponding to a quasi-reversible electrode reactions[46] or show an exponential dependence indicating a diffusion-controlled electrode process.[47] Note that the ratio $I_p f^{-1/2}$ corresponds to the dimensionless net-peak current (Φ) and the $f^{1/2}$ to the resistance parameter (q), where: $\Phi = I_p(nFS\,c^*_{OX})^{-1}(Df)^{-1/2}$, $q = R_\Omega(n^2F^2/RT)S\,c^*_{OX}(Df)^{1/2}$, n is the number of electrons, F is the Faraday constant, S is the electrode surface area, c^*_{OX} is the bulk concentration of the reactant Ox, R_Ω is the resistance of a thin film, f is the SW frequency and D is the diffusion coefficient.

Fig. 2B shows the dependence of the ratio $I_p f^{-1/2}$ on $f^{1/2}$ for the oxidation of 10^{-3} M epinephrine At G and G/PtNP-Chi electrodes, respectively. For both peak pairs, the oxidation of epinephrine occur as a quasi-reversible electrode process at G electrode and under diffusion-controlled at G/PtNP-Chi, as observed in the CV experiments. The obtained results are in good qualitative agreement with the theoretical variation predicted for an EC type mechanism.[48]

Influence of the pH

The influence of the pH value of phosphate electrolyte on the $E^{o'}$ (for CV) or on the E_{pa} (for SWV) was investigated in the range of 4.5- 7.5. The cyclic- and the square-wave voltammograms show a shifts towards negative values of the Ia/Ic and IIa/IIc peaks pairs potentials, if the pH of the solution increases, suggesting that the overall process is proton dependent. A linear relationships of $E^{o'} = a + (p/n)$ pH (for CV) or $E_{pa} = a + (p/n)$ pH (for SWV) were obtained (Fig. 3), for both peak pairs (where: p = number of protons and n = number of electrons involved in the redox reaction). The slopes of the above linear dependencies have values close to the theoretical Nernstian value of 0.059 V/pH which indicate that the electron transfer step is preceded by a protonation with an equal number of protons like the number of electrons involved in the epinephrine oxidation mechanism.[33,40]

Table 3

Electrochemical parameters for the redox behavior of 10^{-3} M epinephrine. Experimental conditions: see Figure 1

pH	CV, v = 50 mV/s Slope of the $E^{o'} = a + (p/n)$ pH R/n		SWV, f = 10 s^{-1} Slope of the $E_{pa} = a + (p/n)$ pH R/n	
	Peak I	Peak II	Peak Ia	Peak IIa
	G electrode			
pH 4 ÷ 5.5	-0.007 ± 0.0087 0.485/ 4	-0.071 ± 0.003 0.9962/ 8	0.027 ± 0.0002 0.99993/ 4	-0.066 ± 0.0007 R = 0.9997/ 8
pH 5.5 ÷ 7.5	-0.057 ± 0.003 0.9973/4		0.062 ± 0.002 0.99771/ 5	
	G/PtNP-Chi electrode			
pH 4 ÷ 5.5	0.045 ± 0.032 0.991/6	0.071 ± 0.015 0.9561/4	0.044 ± 0.002 0.9952/7	0.036 ± 0.003 0.9862/5
pH 5.5 ÷ 7.5		0.105 ± 0.029 0.9312/4		0.057 ± 0.002 0.9983/4

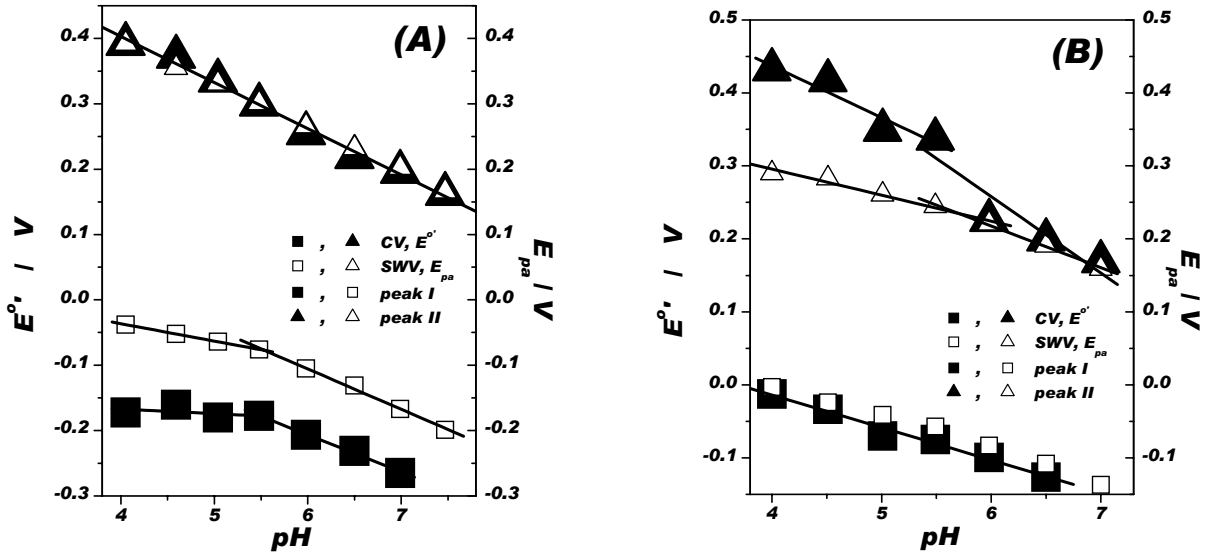


Fig. 3 – Influence of the pH on the oxidation of 10^{-3} M epinephrine at G (A) and G/PtNP-Chi modified electrode (B) investigated by CV (■, ▲) or by SWV (□, Δ). Experimental conditions: electrolyte, 0.1 M phosphate buffer; starting potential, -1 V *vs.* Ag/AgCl,KCl_{sat}; scan rate, 0.05 V/s (CV); step potential, 0.002 V (SWV); amplitude, 0.050 V (SWV); frequency 10 s^{-1} (SWV).

Moreover, a variation of the current intensity of the peak pairs Ia/Ic and IIa/IIc was observed with the increase of the pH of solution, and a maximum value were obtained in the pH range between 6 and 8. Thus, the electrochemical analysis of epinephrine at G and G/PtNP-Chi electrodes was carried out in a phosphate solution of pH 7.[40]

Analytical characterizations

The investigations by square-wave voltammetry is the most advanced and most sophisticated method from the pulse voltammetric techniques and exhibits the advantages of a very sensitive method with a low detection limit for determination of trace amounts of epinephrine in pharmaceutical and clinical samples.[28,49]

Fig. 4 A exhibits the SW voltammograms recorded at bare G electrode for the phosphate buffer solutions of pH 7 containing various concentrations of epinephrine. Fig. 4B presents the variation of the IIa anodic peak current *versus* the concentration of epinephrine at G and G/PtNP-Chi modified electrodes. At bare G electrode the linear range of detection is 0.15 – 1.5 mM epinephrine, with a sensitivity of 70 ± 1.6 mA/M and a detection limit (LOD) of 0.026 mM epinephrine (where R = 0.9964, n =16 points, and the LOD was estimated for a signal to noise ratio of 3). Contrarily, at G/PtNP-Chi modified electrode the linear range of detection is 0.19 - 1.4 mM epinephrine, with a sensitivity of 55 ± 2.6 mA/M and a LOD of 0.016 mM epinephrine (where R = 0.9907, n = 10 points). Although the linear range is quasi similar (Fig. 4B inset), as expected the sensitivity of the G/PtNP-Chi modified electrode are poorly than for bare graphite because of the PtNP-Chi matrix present in the architecture of the modified electrode. However comparing with G electrode, the G/PtNP-Chi modified electrode presents much best analytical parameters, but which are in agreement with the literature date (LOD of 0.034 mM epinephrine at PdNP electrodeposited on glassy carbon electrode),[24] and recommend it as a powerful device for the detection of epinephrine.

At G/PtNP-Chi modified electrode, the dependence between the current and epinephrine concentration leveled off at concentrations higher than 1.5 mM of epinephrine, leading to a possible hyperbolic approach following a Michaelis–Menten kinetic mechanism (Fig. 4B, circle points) because of the presence of PtNP on the electrode surface.

Real sample analysis

In order to evaluate the applicability of the proposed electrode, an attempt was made to determine epinephrine in epinephrine hydrochloride solution in ampoule (specified content of epinephrine is 1.00 mg ml^{-1}), under the

optimized experimental conditions, using the standard addition method in order to overcome possible matrix effects. The method consists in addition of different volumes of standard solution of epinephrine 10^{-2} M to 10 mL of phosphate buffer containing 0.2 μL of ampoule solution. The SWV technique was used to measure the anodic peak potential current at G and G/PtNP-Chi modified electrode (Fig. 5).

The average determination results of epineprine in the ampoule were 0.9 ± 0.06 mg/mL and 1.06 ± 0.03 mg/mL when G/PtNP-Chi modified electrode and G electrode was used, respectively. The results were quite corresponding to the value that was given by ampoule specification and showed that the proposed methods could be efficiently used for the determination of epinephrine in pharmaceutical formulation.

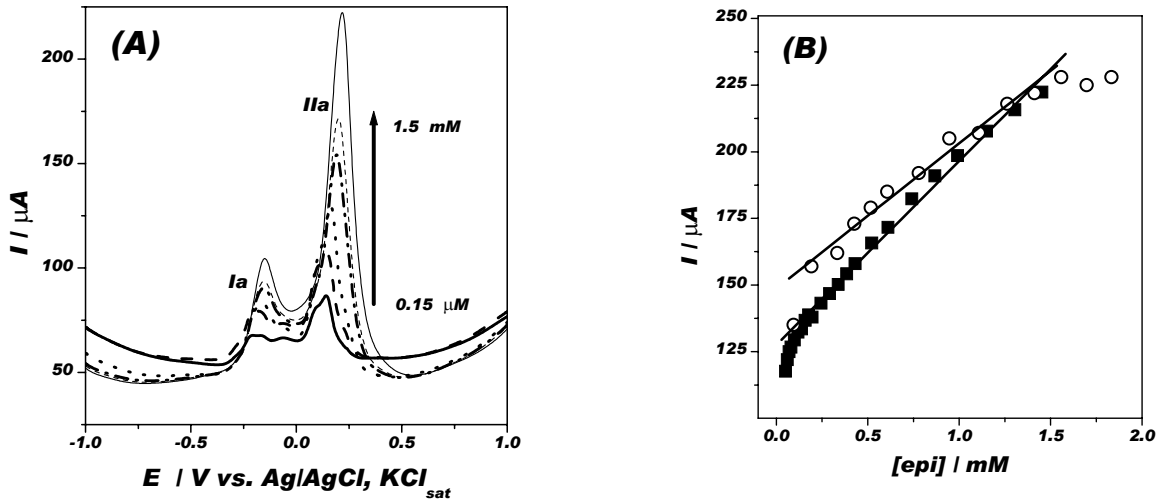


Fig. 4 – SW voltamogramms for increasing concentration of epinephrine at G electrode (A) and the corresponding calibration curves for G (■) and G/PtNP-Chi (O) modified electrode (B). Experimental conditions: electrolyte, 0.1 M phosphate buffer (pH 7); starting potential, -1 V *vs.* Ag/AgCl,KCl_{sat}; step potential, 0.002 V; amplitude, 0.050 V; frequency 10 s^{-1}.

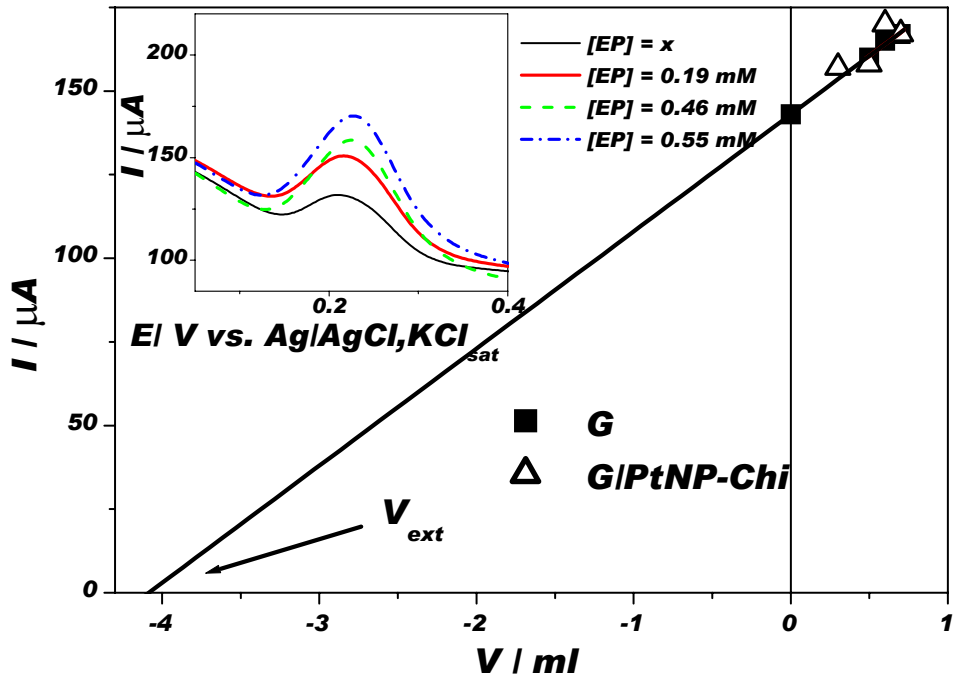


Fig. 5 – Dependency of the current intensity of the peak IIa *versus* volume of 10^{-2} M standard epinephrine solution added. Experimental conditions: see Fig. 4.

CONCLUSIONS

In the present study modified graphite electrode by including PtNP into a polymer matrix of chitosan was prepared by a simple method of evaporation of the solvent. The obtained G/PtNP-Chi modified electrode exhibits good electrochemical parameters comparing with the bare G electrode. The large peak separation obtained with this electrode confirms a quasi-reversible diffusion controlled redox electrode process, the influence of pH validating the well-known $2e^+/2H^+$ mechanism at this type of electrode. Moreover, good analytical parameters like high sensitivity and low detection limit make this modified electrode very suitable for accurate determinations in real samples. The G/PtNP-Chi modified electrode demonstrates that could be successfully employed to the determination of epinephrine in pharmaceutical ampoule.

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